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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SUMITOMO BAKELITE CO LTD

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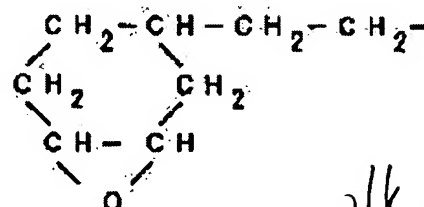
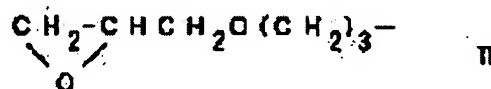
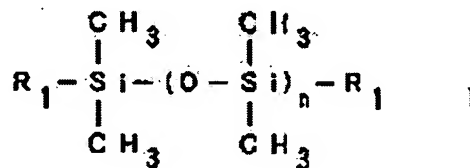
## (54) LIQUID INJECTION SEALING UNDERFILLING MATERIAL

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject material having both stress-reducing properties giving durability to thermal stress and reworkability by incorporating an epoxy resin in a liquid state at normal temperature, which contains a specific epoxy resin in a specific content, with a curing agent and an inorganic filler.

SOLUTION: This material is obtained by containing (A) an epoxy resin in a liquid state at normal temperature with pref. a viscosity of  $\leq 500$  PA.s at 25°C which includes 5-30wt.% of an epoxy resin of formula I [(n)=4(m)+1; (m) is an integer of  $\geq 0$ ; R1 is a group of formula II or formula III] based on the whole epoxy resins and in which the epoxy resin of the formula I [(m) $\geq 1$ ] is included in the

content range of 10-60wt.% based on the whole epoxy resins of the formula I, (B) a curing agent (e.g. bisphenol A) and (C) a spherical inorganic filler (pref. silica with an average diameter of  $\leq 10\mu\text{m}$  and the maximum diameter of  $\leq 30\mu\text{m}$ , etc.). It is possible to remarkably increase both reworkability and reliability of a flip chip mounting-type semiconductor using an organic printed wiring board by applying the resultant material.



2/k DDM ex

No ratio  
No solventspherical  
silica

AN 1998:580198 CAPLUS  
 DN 129:204012  
 ED Entered STN: 11 Sep 1998  
 TI Liquid epoxy resin underfill materials for semiconductor devices  
 IN Wada, Masahiro  
 PA Sumitomo Bakelite Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 6 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C08G059-30  
 ICS C08K007-18; C08L063-00; H01L023-29; H01L023-31  
 CC 38-3 (Plastics Fabrication and Uses)  
 Section cross-reference(s): 76

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 10231351	A2	19980902	JP 1997-33802	19970218
PRAI JP 1997-33802		19970218		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 10231351	ICM	C08G059-30
	ICS	C08K007-18; C08L063-00; H01L023-29; H01L023-31

AB The materials with low stress and excellent reworking properties contain (A) 5-30% (to total epoxy resins) R1SiMe2(OSiMe2)nR1 [I; n = 4m + 1; m ≥ 0; R1 = 3-glycidyloxypropyl, 2-(3,4-epoxycyclohexyl)ethyl], which contain 10-60% those with m ≥ 1, (B) hardeners, and (C) spherical inorg. fillers. Thus, a composition of a bisphenol F-type epoxy resin 70, I (n = 0; sic) 18, I (n = 1; sic) 12, an alkylated diaminodiphenylmethane 35, an antifoaming agent 1, a coupling agent 3, spherical SiO2 (average size 1.7 μm) 60, fused spherical SiO2 (average size 4.9 μm) 150, and carbon 0.5 part was poured in a flip-chip package and cured at 150° for 2 h to give a product showing good reliability and reworkability.

ST silicone epoxy resin underfill semiconductor reworkability

IT Epoxy resins, uses  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (bisphenol F-based; liquid epoxy resin underfill materials for semiconductor devices with low stress and good reworking properties)

IT Polysiloxanes, uses  
 Polysiloxanes, uses  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (epoxy; liquid epoxy resin underfill materials for semiconductor devices with low stress and good reworking properties)

IT Electronic packaging materials  
 (liquid epoxy resin underfill materials for semiconductor devices with low stress and good reworking properties)

IT Epoxy resins, uses  
 Epoxy resins, uses  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (polysiloxane-; liquid epoxy resin underfill materials for semiconductor devices with low stress and good reworking properties)

IT 101-77-9D, Diaminodiphenylmethane, alkyl derivs. 7631-86-9, Silica, uses 25550-51-0, Methylhexahydrophthalic anhydride  
 RL: MOA (Modifier or additive use); PRP (Properties); TEM (Technical or

DERWENT-ACC-NO: 1998-525514

DERWENT-WEEK: 199845

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TITLE: Under-fill material for sealing semiconductor package by  
liquid injection- comprises liquid epoxy resin, curing  
agent and spherical inorganic filler

PATENT-ASSIGNEE: SUMITOMO BAKELITE CO LTD[SUMB]

PRIORITY-DATA: 1997JP-0033802 (February 18, 1997)

PATENT-FAMILY:

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<u>JP 10231351 A</u>	September 2, 1998	N/A	006	C08G 059/30

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
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INT-CL (IPC): C08G059/30, C08K007/18, C08L063/00, H01L023/29,  
H01L023/31

ABSTRACTED-PUB-NO: JP 10231351A

BASIC-ABSTRACT:

An underfill material for sealing by liquid injection comprises a liquid epoxy resin, a curing agent and a spherical inorganic filler. The epoxy resin contains 5-30 wt. % of epoxy resin of formula (I) which contains 10-60 wt. % of the resin of formula (I in which m = 1 or more), n = 4 m+1, m = 0 or more, R1 = -C3H6-glycidyl or -C2H4-3,4-epoxycyclohexyl.

USE - The underfill material is useful for semiconductor package.

ADVANTAGE - The underfill material has high reliability, thermal stress resistance and low stress.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: FILL MATERIAL SEAL SEMICONDUCTOR PACKAGE LIQUID INJECTION COMPRISE  
LIQUID EPOXY RESIN CURE AGENT SPHERE INORGANIC FILL

DERWENT-CLASS: A21 A85 L03 U11

CPI-CODES: A05-A01E2; A06-A00E2; A08-D01; A08-R01; A10-E06; A11-B; A12-E04;  
A12-E07C; L04-C20A;

EPI-CODES: U11-A07;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; D11 D10 D32 D73 D42 D50 D93 D94 D95 F81 F86 ; P0464\*R D01  
D22 D42 F47 ; M9999 M2073

Polymer Index [1.2]

018 ; P1901 P0464 D01 D10 D11 D18 D19 D22 D42 D76 F34 F47

Polymer Index [1.3]

018 ; D11 D10 D24 D22 D34 D77 D42 D50 D94 D95 F81 F86 ; P0464\*R  
D01 D22 D42 F47 ; S9999 S1376 ; M9999 M2073

Polymer Index [1.4]

018 ; P1456 P1445 F81 F86 D01 D11 D50 D82 Si 4A ; M9999 M2175 ;  
M9999 M2073 ; S9999 S1376

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the liquefied impregnation closure under-filling ingredient used for the impregnation closure of a semi-conductor excellent in low stress nature and reworkability.

[0002]

[Description of the Prior Art] With the densification of IC chip, and high integration, wiring is short and the package gestalt of the object for high frequency and the flip mounting method suitable for many pinization is increasing. Since this mounting can carry out direct loading of the chip in the magnitude of a chip size mostly at a printed circuit board, small, a light weight, and thin shape-ization of it are attained. Although the mounting technology to the printed circuit board of a bare chip has been established, since there is variation of tolerance of the chip and substrate by thermal expansion, the restoration reinforcement by the impregnation closure under-filling ingredient is needed. Although the liquefied closure ingredient was used for this flip mounting mold semi-conductor closure, since it was not enough in respect of dependability compared with the hermetic seal mold by the ceramics, the spread of plastic packages was behind. As a cause of a dependability fall of a flip mounting mold semi-conductor, moisture invades from the open air through (1) impregnation closure under-filling ingredient.

(2) Moisture invades from an organic wiring substrate.

(3) An impurity invades from a solder bump.

(4) In case an impregnation closure under-filling ingredient is made to flow into a package under an atmospheric pressure, air bubbles arise, and when heat stress is added, a crack occurs.

(5) Since line coefficients of thermal expansion with a closure ingredient, a semiconductor chip, an organic substrate, and a solder bump differ, when heat stress is added, exfoliation arises in an interface. Thereby, the mechanical damage to a chip occurs in the invasion list of moisture.

\*\* is mentioned. The above problem must be cleared on the occasion of utilization of a liquefied impregnation closure under-filling ingredient. Furthermore, it is expected that said flip chip mounting mold will increase from now on to the so-called application of the multi chip module (MCM) of the type which mounted two or more chips on one substrate. In MCM, when a defect is discovered after an under-filling resin seal, it may heat more than the melting point of a connection ingredient (solder), a chip may be removed (rework), and it may re-mount. Generally, even the adhesion over the chip and the organic substrate in an operating temperature field falls, and the problem of the above (5) becomes easy to generate an impregnation closure under-filling ingredient with easier removal highly [ reworkability ].

[0003]

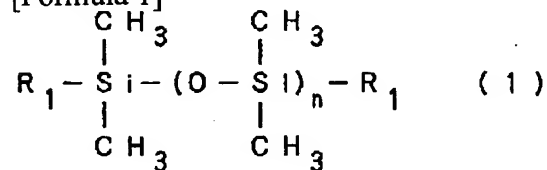
[Problem(s) to be Solved by the Invention] Made in order that this invention may solve the above-mentioned problem of the conventional impregnation closure under-filling ingredient, the place made into the purpose is to offer the impregnation closure under-filling ingredient which combines the low stress nature which can bear heat stress, and reworkability.

[0004]

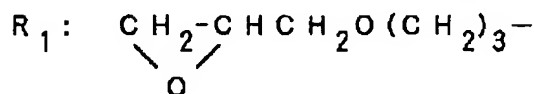
[Means for Solving the Problem] The epoxy resin which this invention consists of a liquefied epoxy resin, a curing agent, and a spherical inorganic filler in ordinary temperature, and the epoxy resin with which an epoxy resin is shown by the formula (1) in [ all ] an epoxy resin contains 30% of the weight from 5 % of the weight, and is shown by the formula (1) is a liquefied impregnation closure under-filling ingredient characterized by  $m = 1$  or more components containing 60% of the weight from 10 % of the weight at least.

[0005]

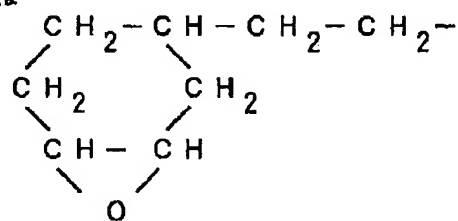
[Formula 1]



(式中、 $n = 4m + 1$  ( $m$  は 0 以上の整数))



または



[0006] The reworkability and dependability of the flip chip mounting mold semi-conductor using an organic printed-circuit board can be sharply raised by using this ingredient.

[0007]

[Embodiment of the Invention]  $m = 1$  or more components contain at least the epoxy resin which the epoxy resin shown by the formula (1) in [ all ] an epoxy resin contains a liquefied epoxy resin 30% of the weight from 5 % of the weight in the ordinary temperature used for this invention, and is shown by the formula (1) 60% of the weight from 10 % of the weight. Although adhesive strength is strong at 5 or less % of the weight, and the epoxy resin shown by the formula (1) in [ all ] an epoxy resin here does not discover reworkability but shows low stress nature at 30 % of the weight or more, an adhesive property falls remarkably. Moreover, if contained more mostly [ when  $m = 1$  or more components contained in the epoxy resin shown by the formula (1) are less than 10 % of the weight ] than 60 % of the weight which reworkability does not discover, bleeding will happen and an adhesive property will fall remarkably. Bleeding can also be suppressed by denaturalizing beforehand in the case of the latter (for example, phenols etc.), and making compatibility high. As for an epoxy resin component, it is desirable that the viscosity in 25 degrees C is 500 or less PA-s. If the viscosity of an epoxy resin component is higher than 500 Pa-s, in case the viscosity of a constituent will become high and will carry out flow impregnation of the under-filling ingredient of a under [ a flip chip mounting mold package ], air bubbles are involved in, or it becomes easy to generate the restoration good to a corner edge, leads to a dependability fall, and is not desirable.

[0008] In the case of a liquefied epoxy resin, in the measurement of viscosity of an epoxy resin, it measures in 25-degreeC with East Machine Industry and a \*\* E mold viscometer, and a Brookfield viscometer at a room temperature. Although it is not the object which will be limited especially if it is with the epoxy resin which satisfies this requirement As resin other than the epoxy resin shown by the formula (1), for example, bisphenol A, By the poly glycidyl ether obtained at the reaction of Bisphenol

F, a phenol novolak, and epichlorohydrin, the object of ordinary temperature, Vinylcyclohexene dioxide, dicyclopentadiene oxide, Alicyclic epoxy like ant cyclic diepoxy-horse mackerel PEIDO, and also n-butyl glycidyl ether, There is a thing like parser tick acid glycidyl ester, styrene oxide phenyl glycidyl ether, buthylphenyl glycidyl ether, the KUREGURISHIJIRU ether, and dicyclopentadiene diepoxide usually used as dilution material of an epoxy resin. These do not interfere, even if it mixes, even when it is independent. Moreover, in order to obtain the liquefied impregnation closure under-filling ingredient which was excellent in dependability, the fewest possible things of ionicity impurities, such as Na<sup>+</sup> and Cl<sup>-</sup>, are desirable [ the epoxy resin which is equal to use ].

[0009] Although it will not be limited especially if the curing agent used for this invention does not influence the dependability as a flip chip, pot life, and liquefied resin viscosity, what has active hydrogen in intramolecular is desirable. as the example -- phenols (for example, bisphenol A and Bisphenol F --) Bisphenol A P, Bisphenol S, Bisphenol Z, dimethyl bisphenol A, The dimethyl bisphenol F, tetramethyl bisphenol A, the tetramethyl bisphenol F Biphenol, tetramethyl biphenol, dihydroxy diphenyl ether, A dihydroxy benzophenone, an o-hydroxy phenol, an m-hydroxy phenol, Polyphenol, such as a p-hydroxy phenol, phenol novolak resin, and orthochromatic cresol novolak resin Tris phenols, such as a trihydroxy phenylmethane and a trihydroxy phenylmethane, primary amine, aromatic series polyamine, an imidazole, etc. are mentioned. These do not interfere, even if it mixes, even when it is independent. Moreover, in order to obtain the liquefied impregnation closure under-filling ingredient which was excellent in dependability, the fewest possible things of ionicity impurities, such as Na<sup>+</sup> and Cl<sup>-</sup>, are desirable [ the amine system curing agent which is equal to use ].

f [0010] As for the spherical inorganic filler used for this invention, it is desirable that the mean particle diameter is [ 10 micrometers or less and a maximum grain size ] 30 micrometers or less. Although there are nitriding aluminum, an alumina, a silica, etc. in an inorganic filler, the field of heat leakage nature and cost to a silica particle is desirable, and it is more desirable if it is a low radiation. Although a configuration has the shape of a globular shape, the letter of crushing, and a flake etc., since reduction-ization of coefficient of linear expansion is attained by high restoration-ization of a filler, the shape of a ball is the best. The addition of a spherical inorganic filler has 50 - 80 desirable % of the weight to all constituents. When it is less than 50 % of the weight, the reduction effectiveness of an above-mentioned coefficient of linear expansion is small, and since the viscosity of the constituent obtained as a result will become high too much and flowability will get worse if 80 % of the weight is exceeded, it is not desirable.

f [0011] The flowability of a liquefied impregnation closure under-filling ingredient is greatly dependent also on the particle size distribution of a filler. Generally distribution is large and a filler with a larger particle size has [ the viscosity of a constituent is low and ] a better fluidity. however, when the filler which contains a big particle size for the purpose of hypoviscosity-izing is used, particle size is big during hardening -- filler sedimentation is carried out, the line coefficient of thermal expansion in a gap becomes uneven, and it is not desirable in respect of dependability. Moreover, the need that a liquefied impregnation closure under-filling ingredient flows the gap between an organic substrate and a chip (Stand OFF:25-150micrometer) to filler particle size must be smaller than Stand OFF. Conversely, since specific surface area will increase if particle size is too small, the fill of a filler cannot be made high. For satisfying the above requirements, mean particle diameter needs to be 0.5 micrometers to 10 micrometers, and a maximum grain size needs to be a filler 30 micrometers or less. It is better for mean particle diameter to have used 3-9 micrometers, and for a maximum grain size to use the filler of particle size distribution 20 micrometers or less more preferably. Moreover, if there is a filler in the range of a claim, even if it will use independently, what was mixed and gave bimodality to particle size distribution does not interfere.

[0012] Even if it uses additives, such as the catalyst for promoting other resin and reactions other than the aforementioned indispensable component if needed, a diluent, a pigment, a coupling agent, a flame retarder, a leveling agent, and a defoaming agent, it does not interfere with the liquefied impregnation closure under-filling ingredient of this invention. With 3 rolls, 2 hot calender rolls, and a vacuum mixer, a liquefied impregnation closure under-filling ingredient carries out distributed kneading, carries out

bottom degassing processing of a vacuum, and manufactures for example, each component, an additive, etc.

[0013]

[Example] An example explains this invention concretely. An example 1-7 and the example 1-7 of a comparison explain concretely. Weighing capacity was carried out according to the formula of Table 1 and 2, with 3 rolls, distributed kneading was carried out, bottom degassing processing of a vacuum was carried out, the liquefied impregnation closure under-filling ingredient was produced, and the following characterization was performed.

(1) The liquefied impregnation closure under-filling ingredient was applied to the front face which formed the solder resist (PSR[ by the solar ink company ]-4000/CA- 40) on the substrate made from bismaleimide-triazine (BT) resin as a bond strength-organic substrate, the silicon chip of a 2x2mm angle was loaded, it hardened in 150 degrees and 120 minutes, and adhesive strength was measured with the push pull gage at the time of the heat in 150 degrees and 250 degrees.

(2) Trial made from low stress nature - Hardening closure of the 15x6x0.3mm (thickness) silicon chip was carried out in 150 degrees and 120 minutes like (1) at the organic substrate with a thickness of 0.5mm, the maximum of the variation rate of the vertical direction was calculated using a surface roughness meter as a scale of low stress nature, and the longitudinal direction of a chip was made into the substitution property.

(3) After making a liquefied impregnation closure under-filling ingredient pour into a flip chip mounting package for 5 minutes on the heating plate of -80 degrees C of restoration sex test, it hardened in oven at 150 degrees C for 2 hours, and the semiconductor package was obtained. The restoration nature inside a package was checked with the supersonic detector (henceforth SAT).

(4) Reliability trial - PCT processing (125 degree-C/2.3atm) and traveler's check processing (-65 degrees C / 30 minutes <- ->150 degree C / 30 minutes 400 cycles) were performed to the semiconductor package produced by (3), and exfoliation with a semiconductor chip and a printed circuit board interface and the existence of a crack were checked in SAT.

(4) Evaluation trial of reworkability - The semiconductor package was produced like (3) and that to which closure resin remained what removed the chip after heating for 5 minutes, and exfoliated the semiconductor package completely on "fitness" and an organic substrate front face on the 250-degree C heating plate was made into the "defect." The number of the flip chip mounting packages used for every evaluation is ten. In addition, a chip size is 15mm angle and the gap with a substrate is 100 micrometers (except for a low stress trial).

[0014]

[Table 1]

		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	実施例 7
組成	液状エポキシ樹脂 A * 1	70	70	95	40	40	40	35
	液状エポキシ樹脂 B * 2	18	18	3				
	液状エポキシ樹脂 C * 3	12						
	液状エポキシ樹脂 D * 4		12	2				
	液状エポキシ樹脂 E * 5				40	40	40	35
	液状エポキシ樹脂 F * 6				9	18	13	18
	液状エポキシ樹脂 G * 7				11	2	7	12
	硬化剤 * 8	35	35	35				
	硬化剤 * 9				80	80	80	80
	硬化促進剤				1	1	1	1
	消泡剤	1	1	1	1	1	1	1
	カップリング剤	3	3	3	3	3	3	3
	シリカ A * 10	60	60	60	60	60	60	60
	シリカ B * 11	150	150	150	150	150	150	150
	シリカ C * 12							
	シリカ D * 13							
特性	カーボン	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	接着強度 @150°C	2300	1800	2400	2000	2600	2100	2400
	接着強度 @250°C	150	120	160	190	210	140	180
	低圧力性	50	40	60	40	55	50	55
	リワーク性	良好	良好	良好	良好	良好	良好	良好
	信頼性	良好	良好	良好	良好	良好	良好	良好
	流動性	良好	良好	良好	良好	良好	良好	良好

[0015] The numeric value of the column of a presentation of a table is the weight section.

\*1 Liquefied epoxy resin A : bisphenol female mold epoxy resin (equivalent 170) \*2 Liquefied epoxy-resin B: It is thing (equivalent 181) \*3 of n= 0 with the epoxy resin of a formula (1). Liquefied epoxy-resin C: It is the epoxy resin of a formula (1) and is the thing (equivalent 329) of n= 1.

\*4 Liquefied epoxy resin D : it is thing (equivalent 477) \*5 of n= 2 with the epoxy resin of a formula (1). The liquefied epoxy resin E:3, 4-epoxycyclohexyl methyl - 3', 4'-epoxy cyclohexane-carboxylic-acid ester (equivalent 126)

\*6 Liquefied epoxy resin F : it is thing (equivalent 192) \*7 of n= 0 with the cycloaliphatic epoxy resin of a formula (1). Liquefied epoxy-resin G: It is thing (equivalent 340) \*8 of n= 1 with the cycloaliphatic epoxy resin of a formula (1). Curing agent : Alkylation diamino diphenylmethane curing agent (equivalent 65)

\*9 Curing agent : Methyl hexahydrophthalic anhydride \*10 silica : It is mean-particle-diameter [ of 1.7 micrometers ], and 8.0 micrometer \*11 of maximum grain sizes silica at a synthetic spherical silica. : It is mean-particle-diameter [ of 4.9 micrometers ], and 16 micrometer \*12 of maximum grain sizes silica



at a melting spherical silica. : It is mean-particle-diameter [ of 7.9 micrometers ], and 40 micrometer \*13 of maximum grain sizes silica at a melting spherical silica. : It is a melting spherical silica and they are the mean particle diameter of 0.3 micrometers, and 4.0 micrometers [0016] of maximum grain sizes.

[Table 2]

		比較例 1	比較例 2	比較例 3	比較例 4	比較例 5	比較例 6	比較例 7
組成	液状エポキシ樹脂 A * 1	97	50	70	35	70	70	70
	液状エポキシ樹脂 B * 2	2	30	29		6	18	18
	液状エポキシ樹脂 C * 3	1	20	1		24	12	12
	液状エポキシ樹脂 D * 4							
	液状エポキシ樹脂 E * 5				35			
	液状エポキシ樹脂 F * 6				6			
	液状エポキシ樹脂 G * 7				24			
	硬化剤 * 8	38	33	35		35	35	35
	硬化剤 * 9				80			
	硬化促進剤				1			
	消泡剤	1	1	1	1	1	1	1
	カップリング剤	3	3	3	3	3	3	3
	シリカ A * 10	60	60	60	60	60	60	
	シリカ B * 11	150	150	150	150	150		
	シリカ C * 12						150	
	シリカ D * 13							210
	カーボン	0.5	0.5	0.5	0.5	0.5	0.5	0.5
特性	接着強度 @150°C	2800	350	2700	800	400	2200	2100
	接着強度 @250°C	1200	50	1100	240	50	170	120
	低応力性	100	48	80	40	50	55	60
	リワーク性	不良	良好	不良	良好	良好	- * 14	- * 14
	信頼性	クラック	剥離	クラック	剥離	剥離	- * 14	- * 14
	流動性	良好	良好	良好	良好	良好	不良	不良

\* 14 : About the examples 6 and 7 of a comparison, the reworkability trial is not carried out in a reliability-trial list for a fluid defect.

[0017] In the example 1 of a comparison, since there are few epoxy resins of the formula (1) contained in [ all ] an epoxy resin, the bond strength in 200 degrees C is high, and inferior to reworkability. In the example 2 of a comparison, since the epoxy resin of the formula (1) contained in [ all ] an epoxy resin is superfluous, although it excels in low stress nature and reworkability, the bond strength in 150 degrees lacks in dependability low. In the epoxy resin shown by the formula (1), since there are few m=1 or more components, the example 3 of a comparison has the high bond strength in 250 degrees C, and is inferior to reworkability. Since m=1 or more components are superfluous, although low stress nature is

shown in the epoxy resin shown by the formula (1) in the examples 4 and 5 of a comparison, an adhesive property is low and is not in practical use level. In the example 6 of a comparison, since the maximum grain size of a filler is large, the fluidity to the gap of a package is bad. Since the example 7 of a comparison has the small mean particle diameter of a filler, its fluidity is bad at hyperviscosity.

[0018]

[Effect of the Invention] When the closure is performed using the liquefied impregnation closure under-filling ingredient of this invention, the high-reliability semiconductor package which shows the low stress nature which can bear heat stress can be obtained, and improvement in the yield is attained with the good reworkability, and the industrial merit of this invention is size.

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[Translation done.]

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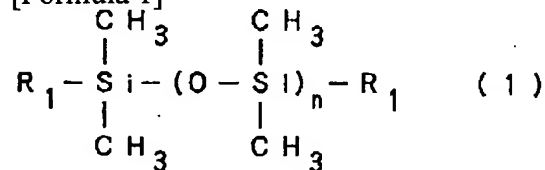
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
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## CLAIMS

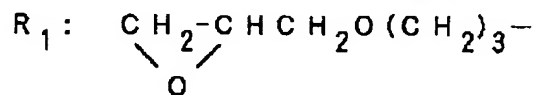
[Claim(s)]

[Claim 1] The epoxy resin which it consists of a liquefied epoxy resin, a curing agent, and a spherical inorganic filler in ordinary temperature, and the epoxy resin with which an epoxy resin is shown by the formula (1) in [ all ] an epoxy resin contains 30% of the weight from 5 % of the weight, and is shown by the formula (1) is a liquefied impregnation closure under-filling ingredient characterized by m= 1 or more components containing 60% of the weight from 10 % of the weight at least.

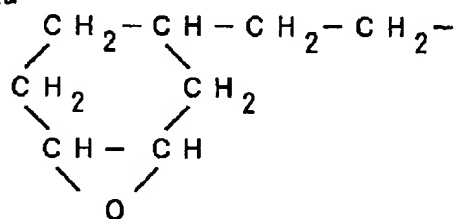
[Formula 1]



(式中、 $n = 4m + 1$  ( $m$ は0以上の整数))



またば



[Claim 2] The liquefied impregnation closure under-filling ingredient according to claim 1 characterized by for the mean particle diameter of a spherical inorganic filler being 0.5 micrometers to 10 micrometers, and a maximum grain size being 30 micrometers or less.

[Translation done.]

(19) 日本国特許庁 (J P)

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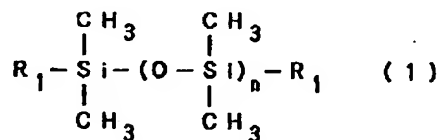
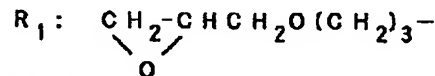
(54) 【発明の名称】 液状注入封止アンダーフィル材料

(57) 【要約】

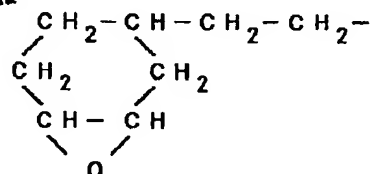
【課題】 熱ストレスに耐えうる低応力性とリワーク性を兼ね備えた注入封止アンダーフィル材料を提供する。

【解決手段】 常温で液状のエポキシ樹脂、硬化剤、球状無機フィラーからなり、エポキシ樹脂が全エポキシ樹脂中に式(1)で示されるエポキシ樹脂が5重量%から30重量%含み、且つ式(1)で示されるエポキシ樹脂は少なくとも $m=1$ 以上の成分が10重量%から60重量%含むことを特徴とする液状注入封止アンダーフィル材料。

【化1】

(式中、 $n=4m+1$  ( $m$ は0以上の整数))

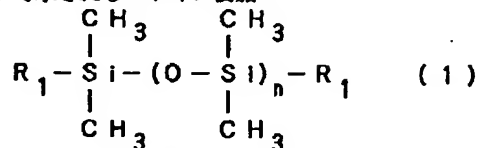
または



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\*は少なくとも $m=1$ 以上の成分が10重量%から60重量%含むことを特徴とする液状注入封止アンダーフィル材料。

【化1】


$$R_1: \begin{array}{c} \text{CH}_2 - \text{CHCH}_2\text{O}(\text{CH}_2)_3 - \\ \quad \backslash \quad / \\ \quad \text{O} \end{array}$$
$$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH} - \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$$

※(5) 封止材料、半導体チップ、有機基板および半田パ  
ンプとの線熱膨張係数が異なるために、熱ストレスが加  
わった際に界面で剥離が生じる。これにより湿気の侵入  
並びにチップへの機械的損傷が発生する。

等が挙げられる。液状注入封止アンダーフィル材料の実

用化に際して、以上の問題はクリアされなければならない

い。更に、1つの基板上に2個以上のチップを実装したタイプのいわゆるマルチチップモジュール(MCM)の用途には、今後前記フリップチップ実装型が増加するこ

30 とが予想されている。MCMでは、アンダーフィル樹脂

封止後に不良が発見された場合、例えば接続材料（半田）の融点以上に加熱しチップを取り外し（リワーク）、再実装する場合がある。一般にリワーク性が高い、すなわち取り外しが容易な注入封止アンダーフィル材料ほど、実用温度領域でのチップおよび有機基板に対する密着性までもが低下し、上記（５）の問題が発生し易くなる。

【発明が解決しようとする課題】本発明は従来の注入封止アンダーフィル材料の上記の問題を解決するためになされたものであり、その目的とするところは熱ストレスに耐えうる低応力性とリワーク性を兼ね備えた注入封止アンダーフィル材料を提供するに有る。

【課題を解決するための手段】本発明は、常温で液状のエポキシ樹脂、硬化剤、球状無機フィラーからなり、エポキシ樹脂が全エポキシ樹脂中に式（１）で示されるエポキシ樹脂が５重量％から３０重量％含み、且つ式

(1)で示されるエポキシ樹脂は少なくとも $m=1$ 以上の成分が10重量%から60重量%含むことを特徴とす

※50

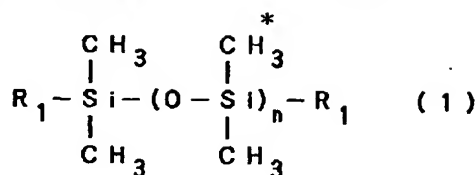
の成分が10重量%から60重量%含むことを特徴とす

(4) 大気圧下で注入封止アンダーフィル材料をパッケージ内へ流動させる際に気泡が生じ、熱ストレスが加わった際にクラックが発生する。

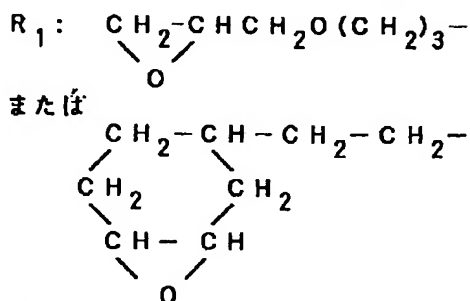
る液状注入封止アンダーフィル材料である。

\*【化1】

【0005】



(式中、 $n = 4m + 1$  ( $m$ は0以上の整数) )



【0006】本材料を用いることにより有機プリント配線基板を用いたフリップチップ実装型半導体のリワーク性および信頼性を大幅に向上させることができる。

【0007】

【発明の実施の形態】本発明に用いられる常温で液状のエポキシ樹脂は、全エポキシ樹脂中に式(1)で示されるエポキシ樹脂が5重量%から30重量%含み、且つ式(1)で示されるエポキシ樹脂は少なくとも $m=1$ 以上の成分が10重量%から60重量%含む。ここで全エポキシ樹脂中に式(1)で示されるエポキシ樹脂が5重量%以下では接着力が強くリワーク性は発現せず、30重量%以上では低応力性を示すが接着性が著しく低下する。また、式(1)で示されるエポキシ樹脂に含まれる $m=1$ 以上の成分が10重量%未満だと、リワーク性が発現しない、60重量%より多く含むとブリードが起これ着着性が著しく低下する。後者の場合、例えばフェノール類などであらかじめ変性し相溶性を高くすることで、ブリードを抑えることもできる。エポキシ樹脂成分は25℃における粘度が500Pa・s以下であることが好ましい。エポキシ樹脂成分の粘度が500Pa・sより高いと組成物の粘度が高くなり、フリップチップ実装型パッケージ中へのアンダーフィル材料を流動注入する際、気泡を巻き込んだり、コーナー端部への充填良が発生し易くなり信頼性低下につながり、好ましくない。

【0008】エポキシ樹脂の粘度測定には、室温で液状のエポキシ樹脂の場合、25°Cにおいて東機産業（株）・製E型粘度計、ブルックフィールド粘度計で測定する。この要件を満たすエポキシ樹脂で有れば特に限定される物ではないが、式（1）で示されるエポキシ樹脂以外の樹脂として例えばビスフェノールA、ビスフェノールF、フェノールノボラックとエピクロルヒドリンとの反応で得られるポリグリシジルエーテルで常温の物、ビニルシクロヘキセンジオキシド、ジシクロペンタ※50

※ジエンオキシド、アリサイクリックジエポキシ—アジペイドの様な脂環式エポキシ、更に $\alpha$ -ブチルグリシジルエーテル、パーサティック酸グリシジルエステル、ステレンオキサイドフェニルグリシジルエーテル、ブチルフェニルグリシジルエーテル、クレグリシジルエーテル、ジシクロペンタジエンジエポキシドの様な通常エポキシ樹脂の希釈材として用いられるものがある。これらは単独でも混合しても差し支えない。また、信頼性の優れた液状注入封止アンダーフィル材料を得るために、使用に耐えるエポキシ樹脂は $\text{Na}^+$ 、 $\text{Cl}^-$ 等のイオン性不純物はできるだけ少ないものが好ましい。

【0009】本発明に用いられる硬化剤はフリップトップとしての信頼性、ポットライフ、液状樹脂粘度に影響しないものであれば特に限定されないが、活性水素を分子内に有するものが望ましい。その例としてはフェノール類（例えばビスフェノールA、ビスフェノールF、ビスフェノールAP、ビスフェノールS、ビスフェノールZ、ジメチルビスフェノールA、ジメチルビスフェノールF、テトラメチルビスフェノールA、テトラメチルビスフェノールF、ビフェノール、テトラメチルビフェノール、ジヒドロキシジフェニルエーテル、ジヒドロキシベンゾフェノン、o-ヒドロキシフェノール、m-ヒドロキシフェノール、p-ヒドロキシフェノール、フェノールノボラック樹脂やオルソクレゾールノボラック樹脂等のポリフェノール類、トリヒドロキシフェニルメタンやトリヒドロキシフェニルメタンなどのトリスフェノール類）、一級アミン、芳香族ポリアミン類、イミダゾール等が挙げられる。これらは単独でも混合しても差し支えない。また、信頼性の優れた液状注入封止アンダーフィル材料を得るために、使用に耐えるアミン系硬化剤はNa<sup>+</sup>、Cl<sup>-</sup>等のイオン性不純物ができるだけ少ないものが好ましい。

【0010】本発明に用いられる球状無機フィラーは、

その平均粒径が $10\mu\text{m}$ 以下、最大粒径が $30\mu\text{m}$ 以下であることが好ましい。無機フィラーには、窒化アルミ、アルミナ、シリカなどがあるが、熱放散性とコストの面からシリカ粒子が好ましく、低放射線であればより好ましい。形状は球状、破砕状、フレーク状等があるが、フィラーの高充填化により線膨張係数の低減化が図られる為、球状が最も良い。球状無機フィラーの添加量は、全組成物に対して50~80重量%が望ましい。50重量%未満だと、上述の線膨張係数の低減効果は小さく、80重量%を越えると結果として得られる組成物の粘度が高くなり過ぎ、流動特性が悪化するため好ましくない。

【0011】液状注入封止アンダーフィル材料の流動特性はフィラーの粒度分布にも大きく依存する。一般に分布が広く、粒径の大きいフィラーほど、組成物の粘度が低く流動性がよい。しかし、低粘度化を目的に大きな粒径を含むフィラーを用いると、硬化中に粒径の大きなフィラー沈降し、間隙中の線膨張係数が不均一となり、信頼性の面で好ましくない。また液状注入封止アンダーフィル材料は有機基板とチップ間の間隙(Stand OFF: 25~150 $\mu\text{m}$ )を流動する必要から、フィラー粒径はStand OFFよりも小さくなければならない。逆に粒径が小さすぎると比表面積が増大するため、フィラーの充填量を高くすることができない。以上の要件を満たすには平均粒径が $0.5\mu\text{m}$ から $10\mu\text{m}$ 、且つ最大粒径が $30\mu\text{m}$ 以下のフィラーである必要がある。より好ましくは平均粒径が3~9 $\mu\text{m}$ 、且つ最大粒径が $20\mu\text{m}$ 以下の粒度分布のフィラーを用いた方がよい。また、フィラーは請求項の範囲で有れば単独で用いても、混合して粒度分布に二峰性を持たせたものでも差し支えない。

【0012】本発明の液状注入封止アンダーフィル材料には、前記の必須成分の他に必要に応じて他の樹脂や反応を促進するための触媒、希釈剤、顔料、カップリング剤、難燃剤、レベリング剤、消泡剤等の添加物を用いても差し支えない。液状注入封止アンダーフィル材料は、例えば各成分、添加物等を三本ロール、二本熱ロール、真空混合機にて分散混練し、真空下脱泡処理して製造する。

【0013】

【実施例】本発明を実施例で具体的に説明する。実施例1~7、比較例1~7で具体的に説明する。表1及び表2の処方に従って秤量し、3本ロールにて、分散混練し真空下脱泡処理をして液状注入封止アンダーフィル材料を作製し、以下の特性評価を行った。

(1) 接着強度-有機基板としてビスマレイミドートリアジン(BT)レジン製基板上にソルダーレジスト(太陽インキ社製PSR-4000/CA-40)を形成した表面に液状注入封止アンダーフィル材料を塗布し、 $2\times 2\text{mm}$ 角のシリコンチップを積載し、 $150^\circ\text{C}$ 、120分で硬化し、 $150^\circ\text{C}$ 及び $250^\circ\text{C}$ における熱時接着力をプッシュプルゲージで測定した。

(2) 低応力性試験-(1)と同様に $15\times 6\times 0.3\text{mm}$ (厚さ)のシリコンチップを厚さ $0.5\text{mm}$ の有機基板に $150^\circ\text{C}$ 、120分で硬化封止し、低応力性の尺度としてチップの長手方向を表面粗さ計を用いて上下方向の変位の最大値を求め、代用特性とした。

(3) 充填性試験- $80^\circ\text{C}$ の熱盤上で液状注入封止アンダーフィル材料をフリップチップ実装パッケージに5分間注入させた後、 $150^\circ\text{C}$ で2時間、オープン中で硬化して半導体パッケージを得た。超音波探傷機(以下、SATという)にて、パッケージ内部の充填性を確認した。

(4) 信頼性試験-(3)で作製した半導体パッケージにPCT処理( $125^\circ\text{C}/2.3\text{atm}$ )、T/C処理( $-65^\circ\text{C}/30\text{分}\rightarrow 150^\circ\text{C}/30\text{分}$  400サイクル)を施して、SATにて半導体チップとプリント基板界面との剥離、クラックの有無を確認した。

(4) リワーク性の評価試験-(3)と同様に半導体パッケージを作製し、 $250^\circ\text{C}$ の熱盤上で半導体パッケージを5分間加熱後チップを剥がし、完全に剥離したものを「良好」、有機基板表面に封止樹脂が残存したものを「不良」とした。各評価ごとに用いたフリップチップ実装パッケージの数は10個である。なお、チップの大きさは $15\text{mm}$ 角で、基板との間隙は $100\mu\text{m}$ である(低応力試験を除く)。

【0014】

【表1】

		実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7
組成	液状エポキシ樹脂A*1	70	70	95	40	40	40	35
	液状エポキシ樹脂B*2	18	18	3				
	液状エポキシ樹脂C*3	12						
	液状エポキシ樹脂D*4		12	2				
	液状エポキシ樹脂E*5				40	40	40	35
	液状エポキシ樹脂F*6				9	18	13	18
	液状エポキシ樹脂G*7				11	2	7	12
	硬化剤*8	35	35	35				
	硬化剤*9				80	80	80	80
	硬化促進剤				1	1	1	1
	消泡剤	1	1	1	1	1	1	1
	カップリング剤	3	3	3	3	3	3	3
	シリカA*10	60	60	60	60	60	60	60
	シリカB*11	150	150	150	150	150	150	150
	シリカC*12							
	シリカD*13							
	カーボン	0.5	0.5	0.5	0.5	0.5	0.5	0.5
特性	接着強度 @150℃	2300	1800	2400	2000	2600	2100	2400
	接着強度 @250℃	150	120	160	180	210	140	180
	低圧力性	50	40	60	40	55	50	55
	リワーク性	良好	良好	良好	良好	良好	良好	良好
	信頼性	良好	良好	良好	良好	良好	良好	良好
	流動性	良好	良好	良好	良好	良好	良好	良好

【0015】表の組成の欄の数値は重量部である。

- \*1 液状エポキシ樹脂A：ビスフェノールF型エポキシ樹脂（当量170）
- \*2 液状エポキシ樹脂B：式（1）のエポキシ樹脂でn=0のもの（当量181）
- \*3 液状エポキシ樹脂C：式（1）のエポキシ樹脂でn=1のもの（当量329）
- \*4 液状エポキシ樹脂D：式（1）のエポキシ樹脂でn=2のもの（当量477）
- \*5 液状エポキシ樹脂E：3,4-エポキシシクロヘキシルメチル-3',4'-エポキシシクロヘキサノールカルボン酸エステル（当量126）
- \*6 液状エポキシ樹脂F：式（1）の脂環式エポキシ樹脂でn=0のもの（当量192）
- \*7 液状エポキシ樹脂G：式（1）の脂環式エポキシ\*

\*樹脂でn=1のもの（当量340）

- \*8 硬化剤：アルキル化ジアミノジフェニルメタン硬化剤（当量65）
- \*9 硬化剤：メチルヘキサヒドロフタル酸無水物
- \*10シリカ：合成球状シリカで平均粒径1.7 $\mu$ m、最大粒径8.0 $\mu$ m
- \*11シリカ：溶融球状シリカで平均粒径4.9 $\mu$ m、最大粒径16 $\mu$ m
- \*12シリカ：溶融球状シリカで平均粒径7.9 $\mu$ m、最大粒径40 $\mu$ m
- \*13シリカ：溶融球状シリカで平均粒径0.3 $\mu$ m、最大粒径4.0 $\mu$ m

【0016】

【表2】



		比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7
組成	液状エポキシ樹脂A*1	97	50	70	35	70	70	70
	液状エポキシ樹脂B*2	2	30	29		6	18	18
	液状エポキシ樹脂C*3	1	20	1		24	12	12
	液状エポキシ樹脂D*4							
	液状エポキシ樹脂E*5				35			
	液状エポキシ樹脂F*6				6			
	液状エポキシ樹脂G*7				24			
	硬化剤*8	38	33	35		35	35	35
	硬化剤*9				80			
	硬化促進剤				1			
	消泡剤	1	1	1	1	1	1	1
	カップリング剤	3	3	3	3	3	3	3
	シリカA*10	60	60	60	60	60	60	
	シリカB*11	150	150	150	150	150		
	シリカC*12						150	
	シリカD*13							210
	カーボン	0.5	0.5	0.5	0.5	0.5	0.5	0.5
特性	接着強度 @150℃	2800	350	2700	800	400	2200	2100
	接着強度 @250℃	1200	50	1100	240	50	170	120
	低応力性	100	48	80	40	50	55	60
	リワーク性	不良	良好	不良	良好	良好	-*14	-*14
	信頼性	クラック	剥離	クラック	剥離	剥離	-*14	-*14
	流動性	良好	良好	良好	良好	良好	不良	不良

\* 14 : 比較例6及び7については流動性不良のため、信頼性試験並びにリワーク性試験は実施していない。

【0017】比較例1では全エポキシ樹脂中に含まれる式(1)のエポキシ樹脂が少ないために、200℃での接着強度が高く、且つリワーク性に劣る。比較例2では全エポキシ樹脂中に含まれる式(1)のエポキシ樹脂が過剰であるために、低応力性とリワーク性に優れているものの、150℃での接着強度が低く且つ信頼性に欠ける。比較例3は式(1)で示されるエポキシ樹脂中にm=1以上の成分が少ないために250℃での接着強度が高く、且つリワーク性に劣る。比較例4、及び5では\*

\*式(1)で示されるエポキシ樹脂中にm=1以上の成分が過剰であるために低応力性を示すが接着性が低く、実用レベルにない。比較例6ではフィラーの最大粒径が大きい為にパッケージのギャップへの流動性が悪い。比較例7はフィラーの平均粒径が小さいために高粘度で流動性が悪い。

40 【0018】

【発明の効果】本発明の液状注入封止アンダーフィル材料を用いて封止を行うと、熱ストレスに耐えうる低応力性を示す高信頼性半導体パッケージを得られ、且つその良好なリワーク性により歩留まりの向上が可能となり、本発明の工業的メリットは大である。

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